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THERMAL DECOMPOSITION REACTIONS OF SOLIDS CONTROLLED BY DIFFUSION AND PHASE-BOUNDARY PROCESSES: POSSIBLE MISINTERPRETATION OF THE MECHANISM FROM THERMOGRAVIMETRIC DATA

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ABSTRACT

A comparative study of phase-boundary and diffusion-controlled reactions has been carried out using thermogravimetric data. The results reported support the hypothesis that a single TG diagram does not allow the determination of whether a solid decomposition reaction is controlled by a diffusion mechanism or governed by the movement of an interface coming from a nucleation process. However, the analysis of both a single TG diagram and an isothermal curve might be a quick and valid way for discerning between these mechanisms. These statements are confirmed by studying the thermal decomposition kinetics of $Ba(OH)_2$ and $CaCO_3$.

INTRODUCTION

Although some methods are available in the literature[1-3] for performing the kinetic analysis of thermogravimetric data of solid thermal decomposition reactions taking place through mechanisms such as: Avrami–Erofeev, Prout and Tompkins, etc., most papers consider such reactions as described by n order reaction mechanism. This is equivalent to considering the reaction rate to be proportional to the nth power of the amount of undecomposed solid, as in the case of a homogeneous reaction.

However, several authors[4,5] have pointed out that the decomposition of a solid is a heterogeneous process, the description of which with homogeneous equations being a meaningless exercise. In fact, the equations developed can have theoretical significance only in those cases where the value of n (reaction order) is 0, 1/2, 2/3 or 1.

Nevertheless, it is a well-established fact that thermogravimetric data of solid thermal decomposition reactions fit very well the reaction order equations. This behaviour might be understood if the established equations needed to perform kinetic analysis of heterogeneous processes in dynamic temperature conditions may also be fitted by some of those available to analyse n order reactions. In this way, it has been shown in former papers[6,7] that in the case of reactions that follow the Prout–Tompkins or Avrami–Erofeev mechanisms, the thermogravimetric data obtained using a constant heating rate must necessarily obey the kinetic equation for a first order reaction. In contrast, this is not true for the data obtained under isothermal conditions.

In the present paper, we attempt, first, to complement these studies by comparing the kinetic equations applicable to the different diffusion mechanisms with those describing a phase-boundary controlled reaction. Secondly, we try to verify the conclusions obtained by studying the thermal decomposition kinetics of $Ba(OH)_2$ and $CaCO_3$, whose mechanisms were previously established[8,9].

EXPERIMENTAL

Materials

$Ba(OH)_2 \cdot 8H_2O$ Merck (Darmstadt) was used, previously dehydrated at 300 °C and also $CaCO_3$ D'Hemio r.a.

Method

The experiments were performed at a vacuum of 10^{-4} Torr, using a Cahn electrobalance Model RG and a heating rate of 11 °C min^{-1}. The temperature was measured with a chromel–alumel thermocouple placed just outside the balance tube as near as possible to the sample.

THEORETICAL

The integral kinetic equation employed in the literature[10] to perform the kinetic analysis of thermal decomposition reactions of solids under isothermal conditions, can be written in a general way as:

$$g(\alpha) = kt \tag{1}$$

where α is the decomposed fraction of the solid after a time t; k the constant rate, related with the temperature by the Arrhenius equation:

$$k = Ae^{-E/RT} \tag{2}$$

and $g(\alpha)$ a function depending on the decomposition mechanism.

In order to carry out the comparative study mentioned above, the expressions for $g(\alpha)$ corresponding to the diffusion mechanisms that will be studied in this paper are included in Table 1, together with those corresponding to 0, 1/2 and 2/3 order reactions.

TABLE 1

ALGEBRAIC EXPRESSIONS OF THE FUNCTION $g(\alpha)$ FOR REACTIONS CONTROLLED BY DIFFUSION AND PHASE-BOUNDARY PROCESSES

Symbol[a]	$g(\alpha)$	*Process controlling the reaction rate*
D_1	α^2	One-dimensional diffusion. Parabolic law.
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion, cylindrical symmetry.
D_3	$[1-(1-\alpha)^{1/3}]^2$	Three-dimensional diffusion, spherical symmetry; Jander equation.
D_4	$(1-\frac{2}{3}\alpha)-(1-\alpha)^{2/3}$	Three-dimensional diffusion, spherical symmetry; Ginstling-Brounshtein equation.
R_1	α	One-dimensional movement of the phase-boundary resulting from the nucleation. Zero order mechanism.
R_2	$1-(1-\alpha)^{1/2}$	Two-dimensional movement of the phase-boundary. Cylindrical symmetry. One-half order mechanism.
R_3	$1-(1-\alpha)^{1/3}$	Three-dimensional movement of the phase-boundary, spherical symmetry. Two-thirds order mechanism.

[a] The symbols of Sharp et al.[11] have been used. This table has been taken, in part, from ref. 12.

If the kinetic analysis is carried out with a TG curve obtained at a constant heating rate, $\beta = dT/dt$, and taking into account eqn (2), the expression (1) becomes:

$$g(\alpha) = \int_0^t k\,dt = \frac{AE}{R\beta}\int_\infty^x \frac{e^{-x}}{x^2}\,dx = \frac{AE}{R\beta}\,p(x) \qquad (3)$$

being $x = E/RT$ and $p(x)$ a function that has been tabulated by several authors[13,14].

An approximate and fast method for calculating the kinetic reaction parameters from eqn (3) has been proposed by Coats and Redfern[15]. This method has been largely used in the literature because it gives reliable results[16,17]. It is based on the quick convergence of the $p(x)$ function, and eqn (3), after taking logarithms and regrouping terms, can be written as:

$$\log\frac{g(\alpha)}{T^2} = \log\frac{AE}{R\beta} - \frac{E}{2.3RT} \qquad (4)$$

If studying a particular reaction, the function $g(\alpha)$ has been properly selected, a plot of the right-hand side of eqn (4) vs. $1/T$ ought to be a straight line from whose slope the activation energy of the reaction can be calculated. Practically, the numerical value of this slope depends on the function $g(\alpha)$, because thermal decomposition of a solid under a linear heating programme occurs in a very narrow range of temperature and the value of log T remains almost constant throughout the reaction.

On the other hand, from Table 1 it can be easily checked that the logarithmic forms of the functions D_1 and D_3 can be obtained from R_1 and R_3, respectively, merely by multiplying these latter by two. Therefore, those reactions of solid thermal decompositions which take place through the parabolic law or Jander mechanism might be erroneously considered as zero or 2/3 order, respectively, if the kinetic analysis were to be performed on the assumption that the reactions of thermal decomposition of solids are *n* order reactions, as habitually made in the literature. Moreover, it is easily deduced tha the activation energy obtained in this way, would be half the value obtained using those diffusion equations.

From Table 1, it is also evident that the g(α) functions for the D_1 and R_1 mechanism, on the one hand, and D_3 and R_3 on the other, are not linearly correlated as the serie of the real numbers are not linearly correlated with their squares. This fact seems to show that using the isothermal method, a straight line would have been obtained only when the g(α) function which describes the correct mechanism is plotted versus the time.

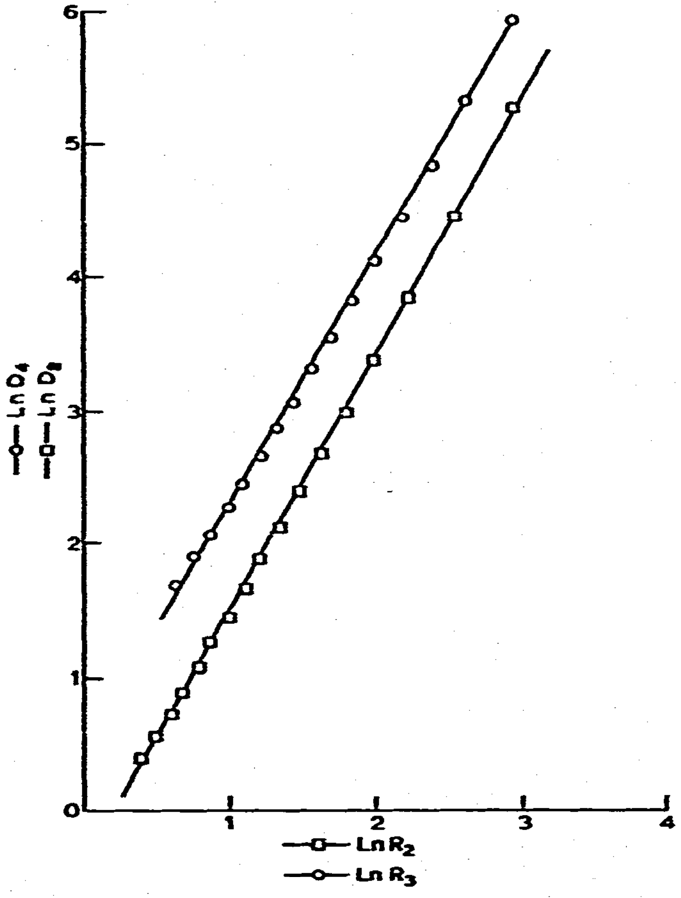

Fig. 1. Relation between the logarithmic forms of the g(α) functions for the mechanisms D_2 and R_2 and also D_4 and R_3.

As regards the functions D_2 and D_4, the existence of any correlation between their logarithmic forms and those of n order reaction is not evident from Table 1. Thus an empirical study has been carried out, whose results are shown in Fig. 1. From these data, using the least mean squares method, the following relations between the logarithmic forms of the functions D_2 and R_2 and also D_4 and R_3 have been obtained:

$$\ln[(1-\alpha)\ln(1-\alpha)+\alpha] = 1.89 \ln[1-(1-\alpha)^{1/2}]+0.40 \tag{5}$$

and

$$\ln[(1-\tfrac{2}{3}\alpha)-(1-\alpha)^{2/3}] = 1.84 \ln[1-(1-\alpha)^{1/3}]-0.46 \tag{6}$$

The calculated linear regression coefficients are 0.9998 and 0.9993, respectively.

Replacing in eqn (4) the log g(a) values of the D_2 and D_4 functions by those established by eqns (5) and (6), and comparing the equations obtained with the ones that result sustituting g(a) by the R_2 and R_3 functions, respectively, it is seen immediately that the reactions taking place through the mechanisms D_2 and D_4 also fit the kinetic equations at programmed temperature for 1/2 and 2/3 order reactions, respectively. The activation energies determined by these latter equations would be 1.8 times less than the experimental values of the diffusion processes.

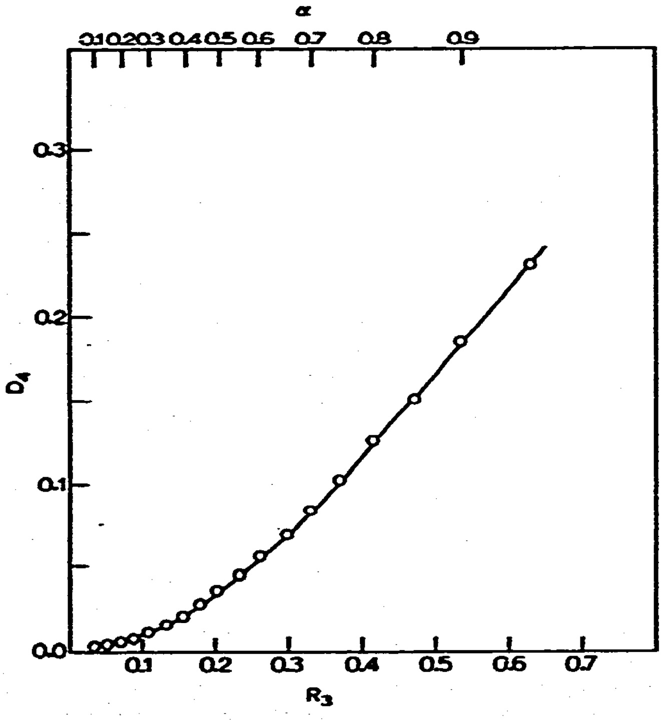

Fig. 2. Relation between the numerical values of the g(a) functions for the mechanisms D_4 and R_3.

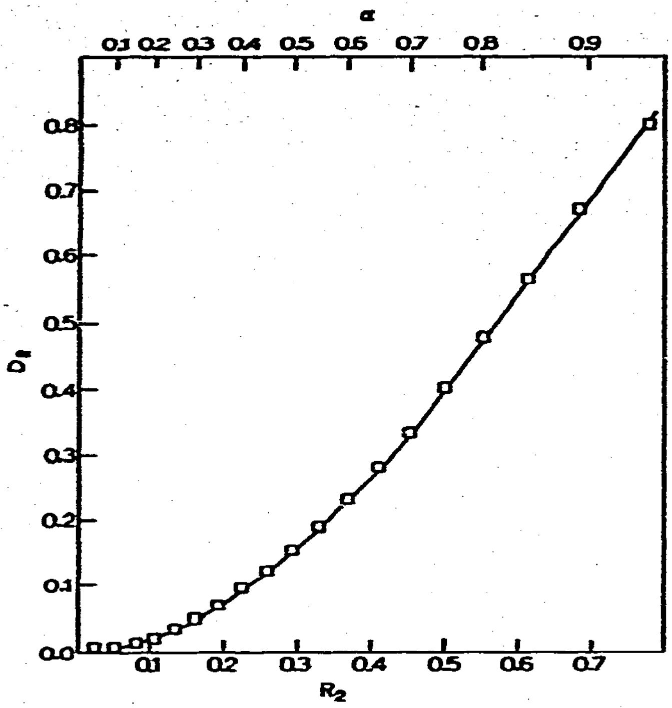

Fig. 3. Relation between the numerical values of the g(α) functions for the mechanisms D_2 and R_2.

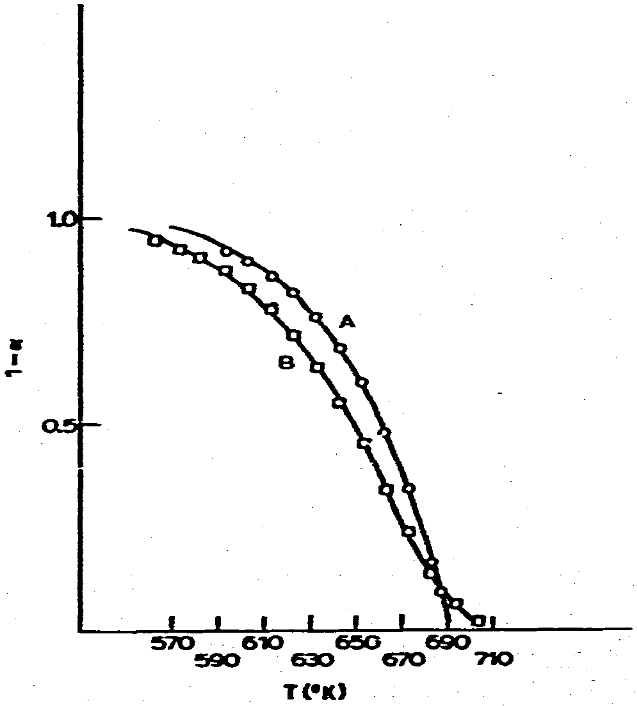

Fig. 4. TG diagrams obtained from eqn (3). (A) D_1 mechanism; (B) D_3 mechanism. In both cases the following parameters have been assumed: $E = 40$ kcal mol^{-1}, $A = 10^{-12}$ min^{-1} and $\beta = 10$ °C min^{-1}.

However, if the kinetic analysis were to be carried out in isothermal conditions, as in the other cases discussed above, this might distinguish experimentally between both series of mechanisms, because the g(α) functions of the mechanisms D_2 and R_2 and also D_4 and R_3 are not linearly correlated (see Figs. 2 and 3).

The validity of these considerations could be checked if the "ideal" TG curves of the mechanisms discussed above were available. These curves can easily be obtained from eqn (3) if the parameters A, E, β and the values of the p(x) function are known. Figure 4 shows the curves for the D_1 and D_3 mechanisms, using the numerical values of the p(x) tabulated by Zsako[14]. For the other parameters the following values have been used: $A = 10^{-12}\,\mathrm{min}^{-1}$, $E = 40\,\mathrm{kcal\,mol}^{-1}$ and $\beta = 10\,^{\circ}\mathrm{C\,min}^{-1}$.

Taking into account the above considerations, the curves D_1 and D_3 have been analysed by means of zero (R_1) and 2/3 (R_3) order mechanisms, respectively. In order to plot $\log[g(\alpha)/T^2]$ vs. $1/T$, the values of α in the interval 0.05–0.95 were taken from the corresponding curves of Fig. 4. This plot is shown in Fig. 5. In both examples, an excellent linearity is obtained (correlation coefficients 0.9999 for both). In either case, the calculated activation en-

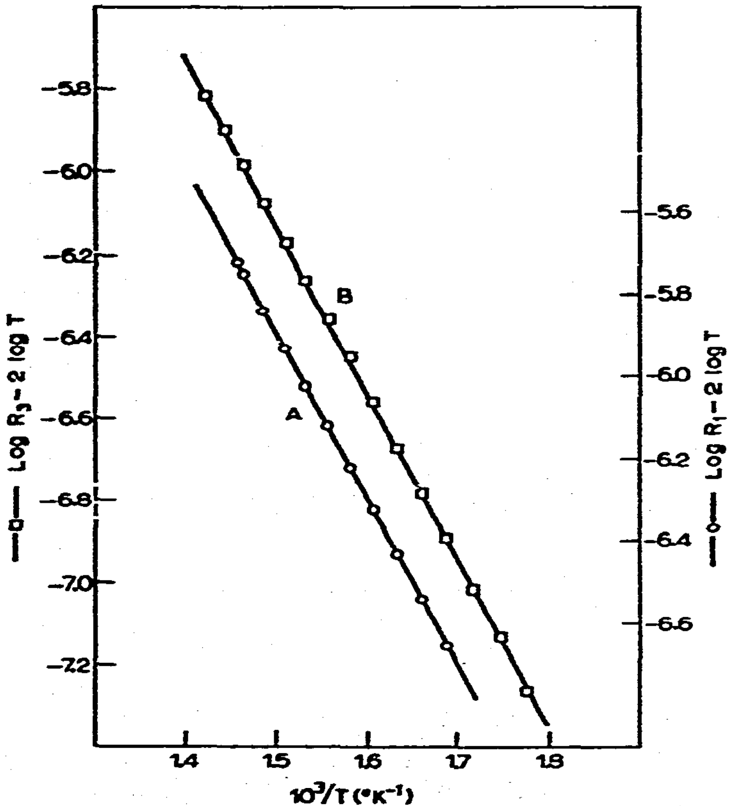

Fig. 5. Kinetic analysis of the TG diagrams of Fig. 4 according to eqn (4). (A) R_1 mechanism, range of α 0.07–0.90; (B) R_3 mechanism range of α 0.05–0.95.

ergy from the slope was 18.5 kcal mol^{-1}. This value lies very close to half of the value used for the construction of the curves, and is in very good agreement with our previous predictions. These results confirm that it is not possible to distinguish between these diffusion and interface mechanisms from a single TG curve, as was deduced above.

Figure 6 shows an "ideal" isotherm at 340 °C, obtained from the diffusion equation:

$$[1-(1-\alpha)^{1/3}]^2 = k \cdot t \tag{7}$$

By using the same numerical values of activation energy and pre-exponential factor as those for obtaining the TG diagrams of Fig. 4, a constant rate of 0.9737.10^{-2} min^{-1} was previously determined from the Arrhenius equation at the above mentioned temperature. The kinetic analysis performed on this isotherm by assuming an R_3 mechanism is also included in Fig. 6. It is clear that the isothermal data calculated according to a diffusion mechanism D_3 do not fit a 2/3 order kinetic equation, as pointed out above.

In the case of the other mechanisms studied in this paper, the conclusion reached above about the theoretical curves used in the analysis hold in the same way. We have omitted this study to considerably shorten the paper.

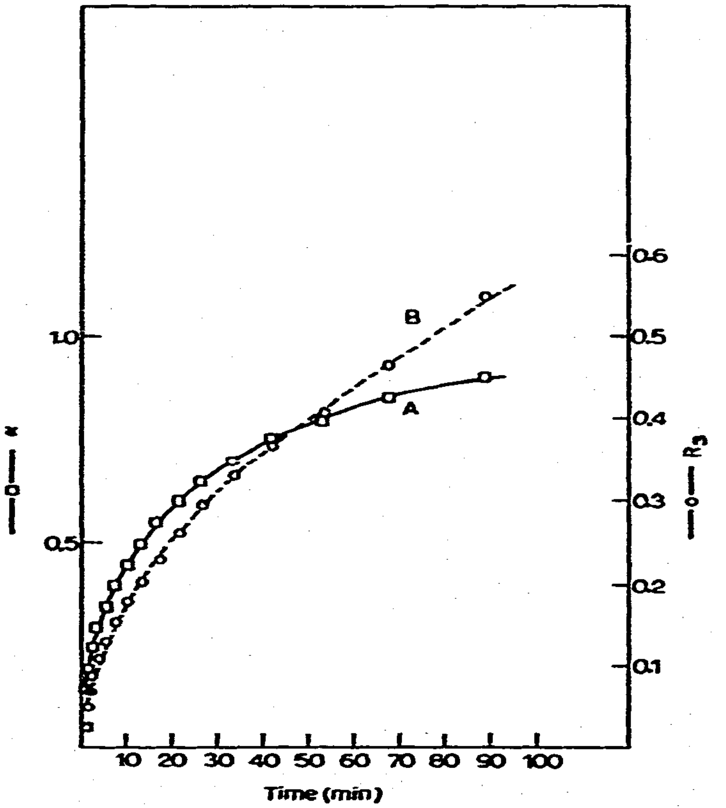

Fig. 6. (A) Isothermal curve calculated from eqn (7) assuming $k = 0.9737 \cdot 10^{-2}$ min^{-1}; (B) kinetic analysis of this isotherm by means of the R_3 mechanism in the α range 0.05–0.95.

To summarise, we conclude from this study that when the thermal decomposition of a solid takes place through diffusion mechanisms D_1 or D_2, the experimental data obtained with a linear heating rate would also fit the interface kinetic equations R_1 and R_2, respectively, and vice versa, being impossible to discern between them with this technique alone. The same can be said as regards the mechanisms D_3 or D_4 and R_3. However, the application of the isothermal method might enable us to distinguish between them.

RESULTS AND DISCUSSION

To check experimentally the above statement, the kinetic study of the TG curves corresponding to thermal decomposition of $Ba(OH)_2$ and $CaCO_3$ is further elaborated.

The kinetics of thermal decomposition of $Ba(OH)_2$ were studied by us in a recent paper[8], and we conclude that a Polanyi–Wigner mechanism (R_1) governs the process. This means that the reaction is independent of the amount of undecomposed reactant. Such a mechanism is in agreement with the fact that this compound decomposes at a temperature above its melting point (about 360 °C) and, therefore, the reaction takes place in the liquid phase. Then, if the BaO coming from the reaction is insoluble in that phase, the "concentration" of $Ba(OH)_2$ does not change and for this reason, the kinetics of decomposition may be described by a zero order mechanism (R_1).

The kinetics of $CaCO_3$ thermal decomposition has been extensively studied and most authors[17, 18] describe the process through the Hume-Colvin "contraction sphere" mechanism, equivalent to a 2/3 order kinetics (R_3).

In Fig. 7 are included the TG curves of $Ba(OH)_2$ and $CaCO_3$, obtained under the conditions described earlier.

The TG curve of $Ba(OH)_2$ has been analysed by means of eqn (4), according to mechanisms R_1 and D_1 (see Fig. 8). As shown in this figure, both models, in accord with earlier considerations, lead to a good linearity (linear regression coefficients: 0.9976 and 0.9978 for R_1 and D_1, respectively). On the other hand, the relation between the calculated activation energies on applying the diffusion parabolic law ($E_{D_1} = 33.5$ kcal mol^{-1}) and the Polangi-Wigner mechanism ($E_{R_1} = 15.5$ kcal mol^{-1}) lies very near two, in good agreement with the earlier deductions.

For $CaCO_3$, the results obtained from the kinetic analysis of the TG diagram of Fig. 7, according to mechanisms R_3, D_3 and D_4 are shown in Fig. 9. It can be seen that the experimental data fit well each of the three kinetic models (linear regression coefficients: $r_{R_3} = 0.9996$, $r_{D_3} = 0.9977$, $r_{D_4} = 0.9979$). On the other hand, the calculated activation energies from the slopes of the straight lines of Fig. 9 are $E_{R_3} = 40$, $E_{D_3} = 80$ and $E_{D_4} = 73.7$ kcal mol^{-1}, values which are in agreement with the relation deduced above.

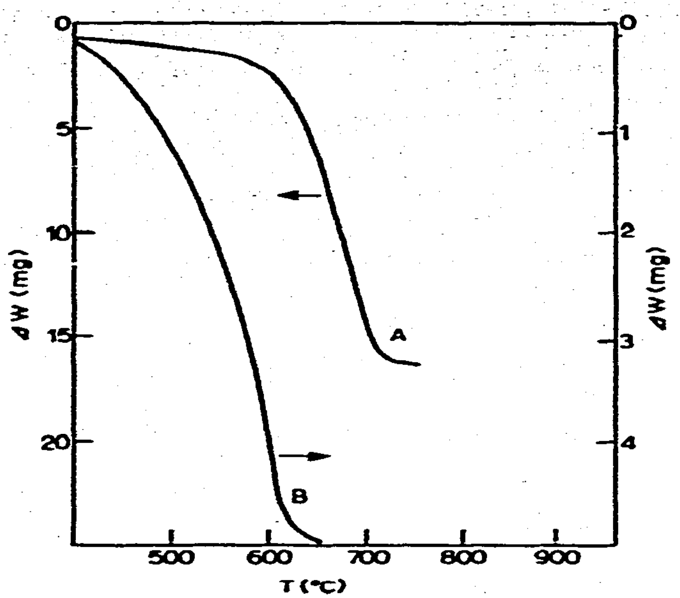

Fig. 7. TG diagrams. (A) $CaCO_3$; (B) $Ba(OH)_2$.

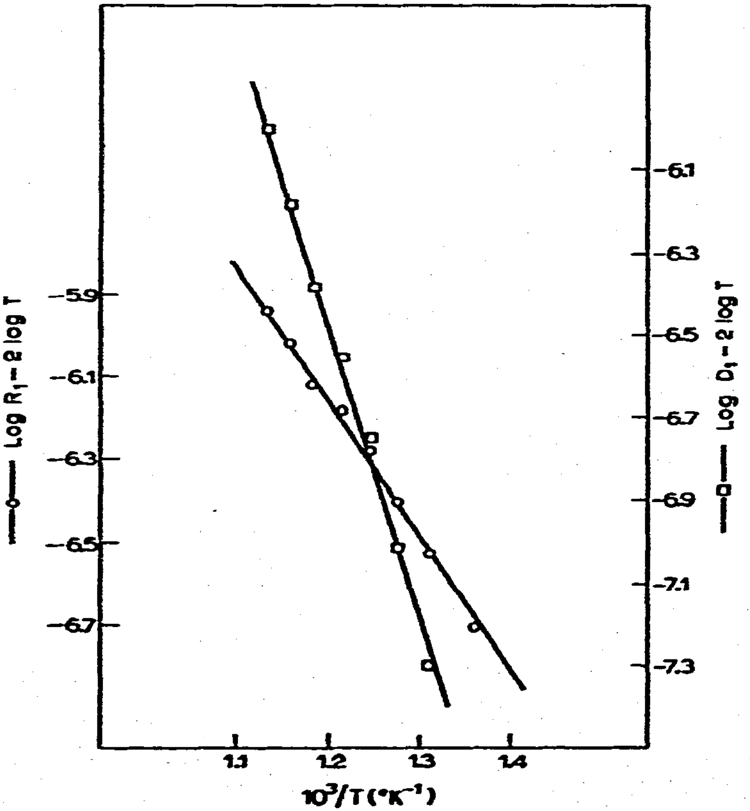

Fig. 8. Data of decomposition of $Ba(OH)_2$ analysed according to mechanisms R_1 and D_1. Range of α 0.10–0.90.

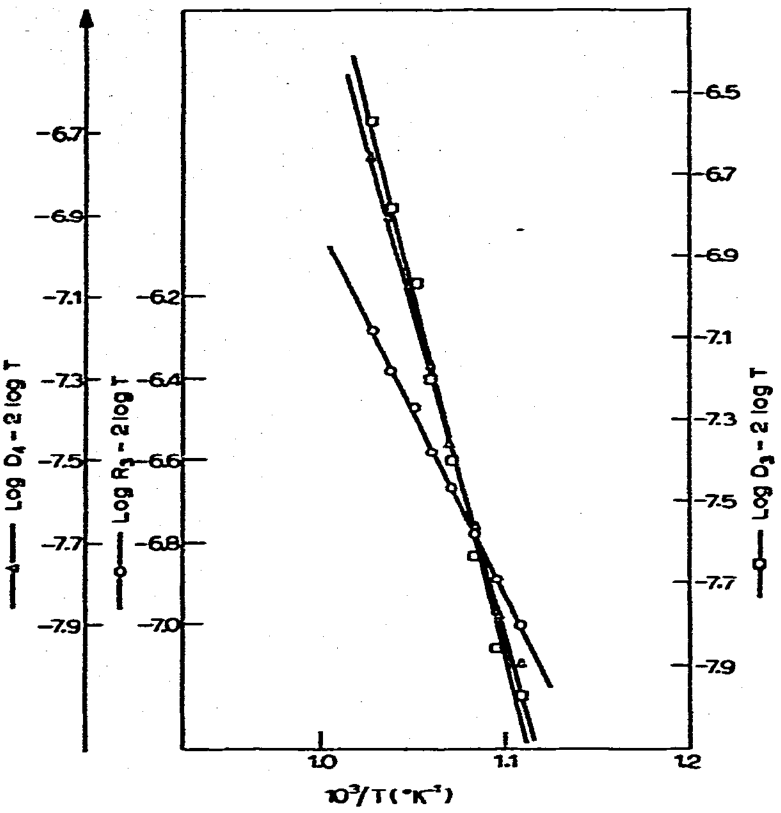

Fig. 9. Data of decomposition of $CaCO_3$ analysed according to mechanisms R_3, D_3 and D_4. Range of a 0.20–0.90.

In order to determine if it is possible to discern between these mechanisms using an isothermal curve, the isothermal decomposition of $CaCO_3$ at 660 °C has been carried out (see Fig. 10). The calculated values for the $g(a)$ function corresponding to R_3, D_3 and D_4 mechanisms from the values of such a diagram, are plotted against the time in Fig. 11. As can be seen from this figure, only the function corresponding to R_3 mechanism shows a good linear correlation with the time ($r = 0.9995$). We conclude then that the reaction takes place through the mechanism named R_3 in Table 1.

In conclusion, the results described support the hypothesis, established before, that a single TG diagram is unable to distinguish between a mechanism governed by diffusion processes and those controlled by interface processes. The same conclusion was reached in previous papers[6,7] with regard to the impossibility of discerning between the reactions described by a first order kinetic equation and those controlled by the Avrami–Erofeev and Prout–Tompkins mechanisms.

Nevertheless, from this paper and the references[6,7] we conclude that the simultaneous kinetic analysis of a TG and an isothermal curve can constitute

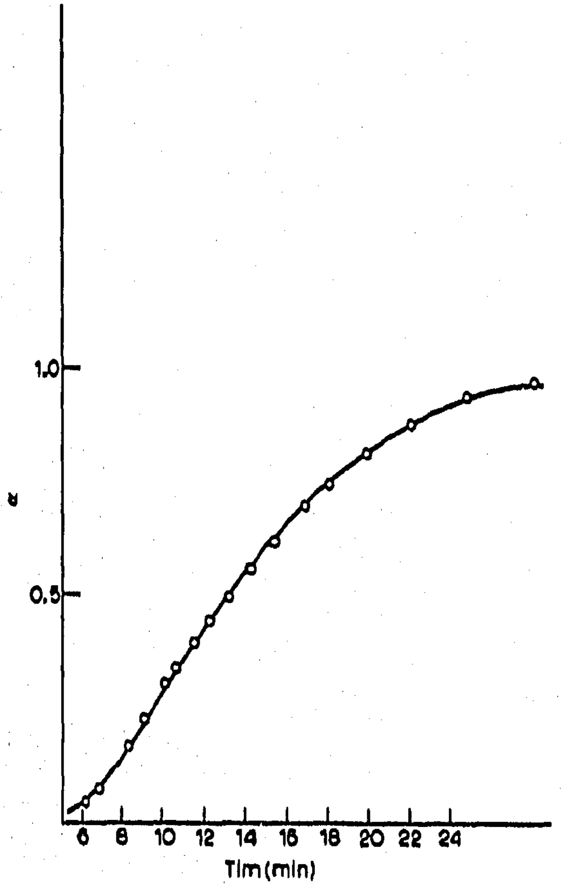

Fig. 10. Isothermal curve of $CaCO_3$ at 660 °C.

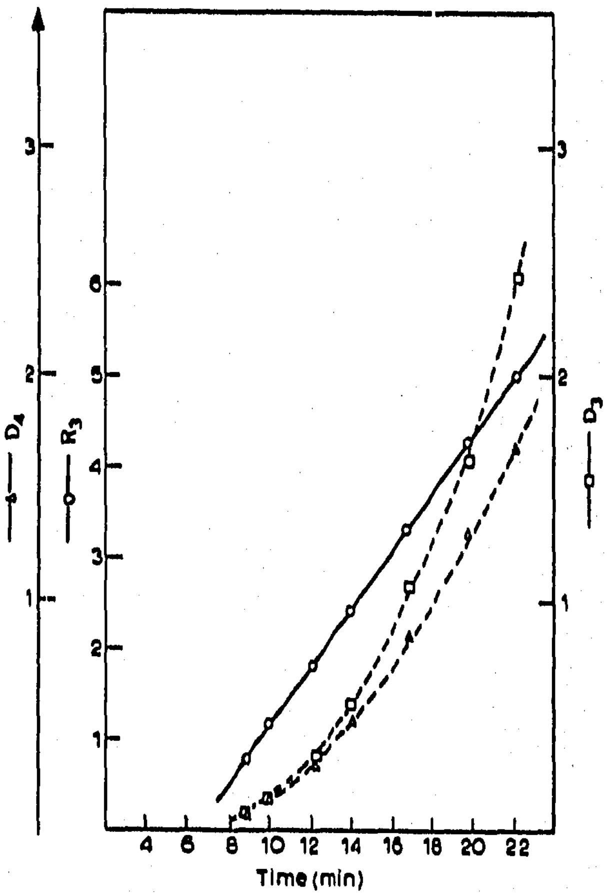

Fig. 11. Data of the isothermal curve of Fig. 10 analysed according to mechanisms R_3, D_3 and D_4. Range of α 0.20–0.90.

an effective and fast method for determining the reaction mechanism, activation energy and frequency factor of the process.

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